Thermodynamics And Kinetics of Materials

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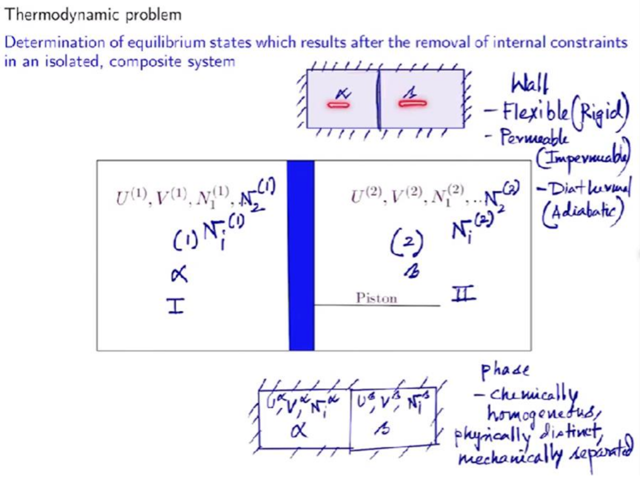
Lecture 9

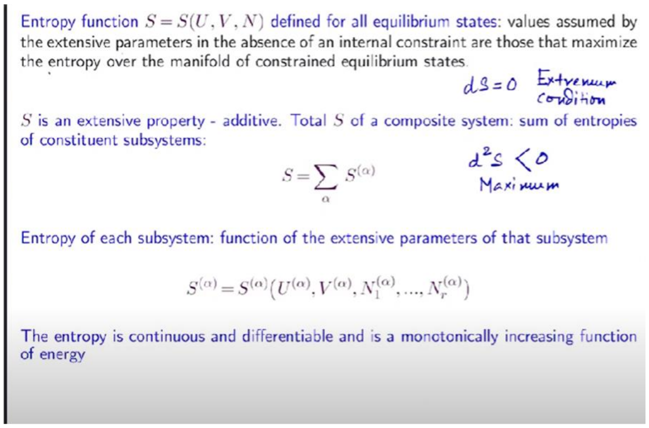
Third Law, Absolute Zero, and Other Energy Functions

So, in the previous lecture we looked at the thermodynamic problem, we defined thermodynamic problem but we told that the central problem is to determine equivalent states of a composite of an isolated composite system containing several subsystems that are separated by wall. So it is an isolated composite system that is overall the system is isolated that means it cannot exchange matter and energy with the surrounding. However, the system is a composite system that contains subsystems like alpha and beta and the substance are separated by wall. The wall initially has this internal constraints such as rigidity, impermeability and adiabatic, right. Adiabatic means it does not allow heat transfer. Then if you remove these internal constraints you want to see what will be the equivalent states, how the equivalent state of alpha and beta will be defined.



Thermodynamic problem

Determination of equilibrium states which results after the removal of internal constraints in an isolated, composite system



Entropy function $S = S(U, V, N)$ defined for all equilibrium states: values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

$dS = 0$ Extremum condition

S is an extensive property - additive. Total S of a composite system: sum of entropies of constituent subsystems:

$$S = \sum_{\alpha} S^{(\alpha)}$$

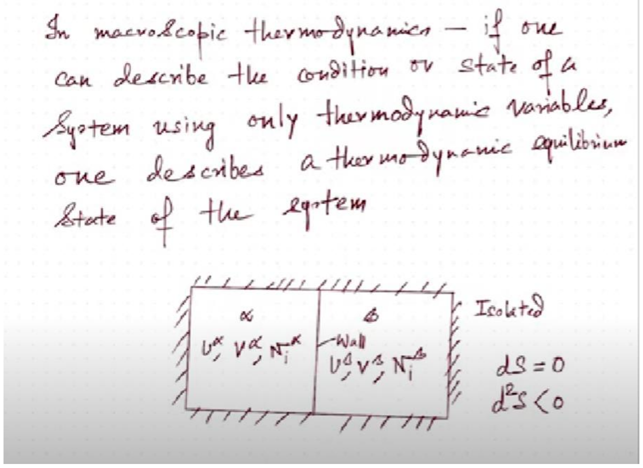
$d^2S < 0$ Maximum

Entropy of each subsystem: function of the extensive parameters of that subsystem

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, ..., N_r^{(\alpha)})$$

The entropy is continuous and differentiable and is a monotonically increasing function of energy

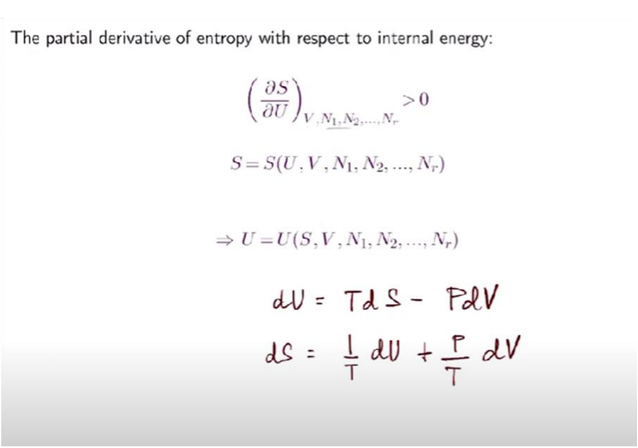
Now the equivalent states will be defined in terms of, you can define in terms of temperature, pressure, you can define also in terms of extensive variables like u, v, n, right. So now comes the first postulate where we define this entropy function which is a function of extensive parameters u, v and n and we tell that the entropy of each sub system is a function of extensive parameters of that sub system and we tell entropy is an additive function that is an extensive property in detail and we tell that the values assumed by this extensive parameters u, v and n in the absence of any internal constraint are those that maximize the entropy of the manifold of constraint between states. That means the values assumed by u, v and n, n1, n2, n3 in difference of systems are the, are those values in absence of any internal constraint are those values that will maximize the entropy, right. Now if you think the total entropy of the system, right, of the composite system. Now when I talk about maximizing we are talking about extremizing a function, right. When we extremize a function first thing that we do is we check that the function like for example here the function is s so ds has to be equal to 0, right that is the extremum condition and that is what we solve and then we check whether this extremum condition corresponds to the condition that is extremum whether it is, whether the second derivative that is d2s is less than 0 or greater than 0. If it is less than 0 then definitely it is maximum. If it is greater than 0 then it is a minimum, right. So if we tell this d2s is less than 0 that means entropy is maximized and in the, when entropy is maximized the equilibrium state described by this values of this extensive parameters in the subsystems are the, will give us the equilibrium condition or the equilibrium between phases or equilibrium between the subsystems, right that is the ideal. So that is the most, that is the key problem or central problem of phase equilibrium, right that is the central problem of phase equilibrium. Now and I also told that see if you have this subsystems, the subsystems are, we can call the subsystems as phases because these subsystems are chemically homogeneous, right and physically they can be considered as chemically homogeneous, physically distinct that is have distinct mechanical properties like density and so on and they are also mechanically separable, right, mechanically separable. So these are your phases and phase and subsystem I will show that the phase that we are talking about and we are talking about multiphase. So in multiphase is nothing but like, but subsystems separated by these boundaries or phase boundaries or wall and this wall basically you can impose constraints on them and then you can remove the constraints or relax the constraints and you can find out the equilibrium state. Now one thing you have to remember that in macroscopic thermodynamics, in macroscopic means the way we are talking about, right, we have not yet connected it to the microscopic, we have tons of molecular interpretation but we will go further into that but before we go into connecting the microscopic world of atoms and molecules with the macroscopic thermodynamics quantities we have to tell this that in macroscopic thermodynamics or, right, in macroscopic thermodynamics if one can describe the condition or state, right, condition or state of a system, right, using only thermodynamic variables, they can be extensive variables, they can be intensive variables but if we can describe the state of a system by using only thermodynamic variables then basically what we are describing, so if one can describe the condition, also your system is using only thermodynamic variables, what you are basically describing is a thermodynamic.



In macroscopic thermodynamics — if one can describe the condition or state of a System using only thermodynamic variables, one describes a thermodynamic equilibrium State of the system

$$dS = 0$$

$$d^2S < 0$$



The partial derivative of entropy with respect to internal energy:

$$\left(\frac{\partial S}{\partial U}\right)_{V, N_1, N_2, \ldots, N_r} > 0$$

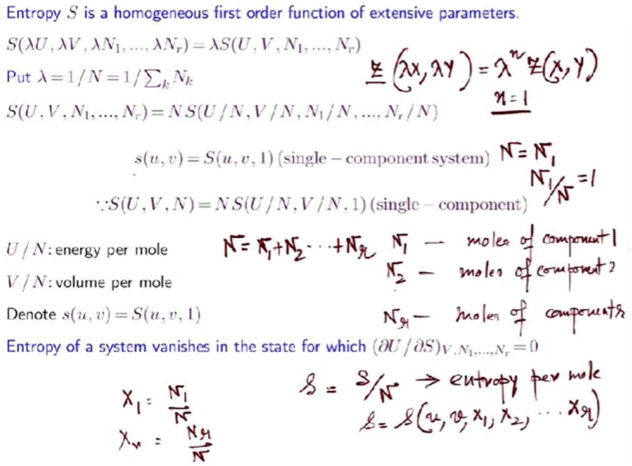
$$S = S(U, V, N_1, N_2, \ldots, N_r)$$

$$\Rightarrow U = U(S, V, N_1, N_2, \ldots, N_r)$$

$$dU = TdS - PdV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

So if one can describe that, so basically that is equivalent to, this is basically the equilibrium state. Now this equilibrium state is in, so one of the equilibrium states, it can be a constrained equilibrium, it can be an unconstrained equilibrium, unconstrained equilibrium is the one where you have removed all constraints, right, you have removed the constraints that you impose in the world if you remove that but whatever it is, either constraint or unconstrained, if we can describe the state of a system using only thermodynamic variables then what we describe, one basically describes a thermodynamic, so it is one equilibrium, so it may be a constrained equilibrium but it is a one thermodynamic equilibrium state of a system. And therefore, when I talk about this axiom of maximization of entropy, what I am talking about is that you have overall there is an isolation, overall the system is isolated, so what I mean, in this symbol, so let us see, I will write this marks here on the boundary, what does this mean, this is, hashes mean basically that this means that overall the system is isolated, right, overall it is isolated from the surroundings, right, but this is the wall, right, wall and you remove in terms of constraints on the wall, so that means you make the wall flexible, you make the wall permeable to the external matter and also diathermal that is your light state of the machine, then you have say for example this is alpha and beta, so which contains u alpha, which contains type of u alpha, v beta and say Ni alpha and here it is u beta, v beta and Ni beta, these values, ok, in absence of this internal constraints, are the values, these values will basically maximize the entropy, so when I tell maximize the entropy that means for these values, ds of the overall system, the overall isolated system will be equal to 0, right, that is the first condition, that is the extremum condition, then you can go to the second condition that is d2s will be less than 0, right, so that it means that entropy is maximized. Now comes the another thing that we told that it has to be continuous and differentiable and monotonically increasing function of energy, right, it is a continuous function of energy, right, s is a continuous function of energy, it is a monotonically increasing function of energy, that is del s del u has to be greater than 0, right, so the partial derivative is greater than 0 and it is continuous and differentiable that means if I know s as a function of u, v and n, right, if I know s as a function of v and n, I can also consider u as a function of s, v and n. By the way, we have done that, say for example, when we have written, so for a single component system when we have written du equals to p ds minus p dv, that is the combined second or first and second law, we could express ds as 1 by p du, right, ds is 1 by p du plus p by t plus p by t dv, right, so both are possible, right, you can write u as a function of s and v and s as a function of u and v because s itself is a continuous and differential function of the energy, not only that, s is a monotonically increasing function of u, right, del s del u has to be greater than 0, right, when v and all the species small number are kept constant, del s del u has to be greater than 0. Another thing, since it is an extensive parameter, since it is an extensive parameter and it is a function of other extensive parameters u vn, now you can think of s as a homogeneous first order function, right, this is called homogeneous first order function, s itself is an extensive variable, that is why it is a homogeneous first order function of extensive parameters, that means s is a function of u vn1 into nr, right, now if I multiply u by lambda u, means I am just basically using lambda as the multiplication of the parameter, so I am changing u to lambda u, v to lambda v, n1 to lambda n1, so lambda can be fraction, lambda can be a whole number like if I put lambda equal to 2u, say for example s, so if I think of something s and instead of u I am telling it is 2u, 2v and say 2n1, so it is a binary system say 2n2 is the same as writing 2s, 2s uv, n1 and n2, that means if I have changed the mole number by twice, mole number of each species two times and u has become 2u and v has become 2v, so I have basically extended, means I have basically changed the extent of the system, right, instead of u I have doubled it to 2u, instead of v I have doubled it to 2v, even the mole numbers of each species have been doubled, then basically this means the entropy itself has been doubled, right, so that is the idea, so it is a homogeneous first order function, so this is basically what we are trying to say here is this, this lambda basically, it is, so if I tell homogeneous nth order function then it is lambda to the power n, here n equal to, now if I tell homogeneous first order, so if I tell this way, say z, z is a function x and y and I am telling that z is a function of a homogeneous nth order function of x and y and if I just multiply lambda, lambda y, this will basically give me lambda to the power n z, now it is first order that means n equal to, right, so z is a homogeneous first order function of x and y, there is a first order function of x and y, right, so here n equal to 1. Now let us put lambda equal to 1 by n, n is the, say n is basically the total number of moles, right, so you have n 1, moles of species 1, moles of species 1 are component 1 and then n 2, moles of, let us call this component, moles of component 1 is a chemical component 1 and n 2, moles of component 2, similarly we have n r, moles of component r, then the total number of moles is n, which is n 1 plus n 2 plus delta, now I have put lambda equal to 1 by n, which is basically 1 by summation n k, where summation over k and k goes from 1 to r, right, now that is then s, so as I told, see if you look at this definition, s of lambda u and all these things is basically lambda s uv n 1, n 2, n i, so here it will be s of uv n 1, n 1, here it will be basically, so I have to just put, I can write this as 1 by n s uv n 1, n 2, now you see what we are writing it as, this lambda is coming here, lambda is coming here, so this is basically 1 by n, so you can write this as s u by n, v by n, n 1 by n, n r by n and then you have also n here because 1 by n has to be multiplied, right, so n into 1 by n is 1, right, so basically what we are telling is s uv n 1 into n r, then immediately follow that we have this 1 by n, here also 1 by n, here also 1 by n and here there should be an n because lambda itself is 1 by n, right, lambda itself is 1 by n, so now if that is the definition, now you can think of this small s uv, say for example, you have a single component system, if you have a single component system N, capital N is nothing but n 1, right, you have only one component, so n 1 by n is basically equal to 1 because n 1 equal to n, right, you have a single component system, so the small s is basically entropy per mole, right, because there is a total number of moles, right, entropy per mole and is a function of u, small u, small u is internal energy per mole, small v is volume per mole, right, volume per mole which is equal to capital S, u small, function of small u small v and 1, right, so basically what we are telling is that since this expression is true, right, because n by n is 1 and u by n v by n, so for a single component system the molar entropy is a function of molar internal energy and molar volume and this is just going to be as a function of molar energy and molar volume, right, that is the idea, so u by n is energy per mole, so S, so what we are telling is S by n is entropy per mole and we are writing it as small s and small s is called small s, let me use small s as this and small s is capital S by capital N, capital S is your expensive parameter, small s is not an expensive parameter, it is per mole, right and small s is a function of small u and small v, where small u indicates internal energy per mole and small v indicates volume per mole and we could have written x1, x2, so if it is a multi component system it would have been u v and here it would have been x1, x2 these are the mole fractions, right, xr, where x1 is equal to n1 by n and xr is equal to nr by n, right and the very important thing that comes in that is the third law basically states what that entropy vanishes, right, for a perfectly this line, for perfectly this line substances at absolute zero entropy vanishes, what we are telling here is entropy of system vanishes in the state for which del u del s, v n1 into equal to 0. Now, what is del u del s? Now, if you look at that we have already shown that, so when we wrote du equals to del u del s and v ds was del u del v ds, s, v and this we wrote as ds minus dv and as you can see del u del s v is nothing but and what we are telling that entropy vanishes in the state for which del u del s v is 0, right. Now, only thing is I have added another potential that is called the chemical potential, right, so p is your mechanical potential, p is your thermal potential and so we have added another mu dn, where mu is your chemical potential and now it becomes v n and here it becomes s comma m, right, so here it is s n. Now, this is t, so we are telling that s vanishes or s becomes 0 when del u del s or t is equal to 0 if del u del s v n which is equal to t is equal to 0 then s equal to 0 for perfectly crystalline substances, right.



Entropy S is a homogeneous first order function of extensive parameters.

$S(\lambda U, \lambda V, \lambda N_1, \ldots, \lambda N_r) = \lambda S(U, V, N_1, \ldots, N_r)$

$\underline{z}(\lambda x, \lambda y) = \lambda^n z(x, y)$

$\underline{n=1}$

Put $\lambda = 1/N = 1/\sum_k N_k$

$S(U, V, N_1, \ldots, N_r) = N S(U/N, V/N, N_1/N, \ldots, N_r/N)$

$s(u, v) = S(u, v, 1)$ (single − component system) $N = N_1$

$N_1/N = 1$

$\because S(U, V, N) = N S(U/N, V/N, 1)$ (single − component)

U/N: energy per mole

V/N: volume per mole

Denote $s(u, v) = S(u, v, 1)$

$N = N_1 + N_2 \cdots + N_r$

N_1 — moles of component 1

N_2 — moles of component 2

N_r — moles of components

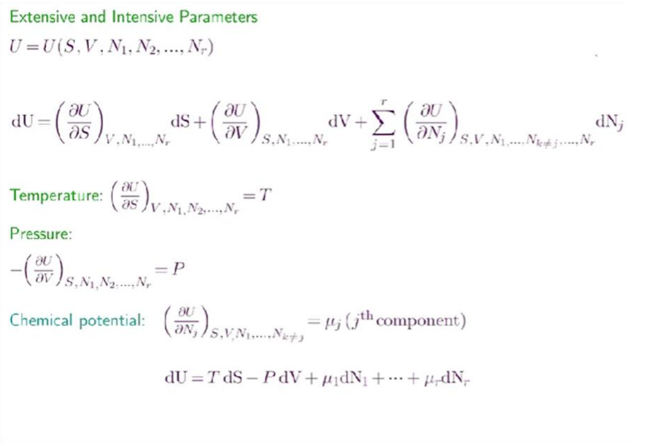
Entropy of a system vanishes in the state for which $(\partial U/\partial S)_{V, N_1, \ldots, N_r} = 0$

$s = S/N$ → entropy per mole

$s = s(u, v, x_1, x_2, \ldots x_r)$

$x_1 = \frac{N_1}{N}$

$x_r = \frac{N_r}{N}$



Extensive and Intensive Parameters

$U = U(S, V, N_1, N_2, \ldots, N_r)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_1, \ldots, N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1, \ldots, N_r} dV + \sum_{j=1}^{r} \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_1, \ldots, N_{k \neq j}, \ldots, N_r} dN_j$$

Temperature: $\left(\frac{\partial U}{\partial S}\right)_{V, N_1, N_2, \ldots, N_r} = T$

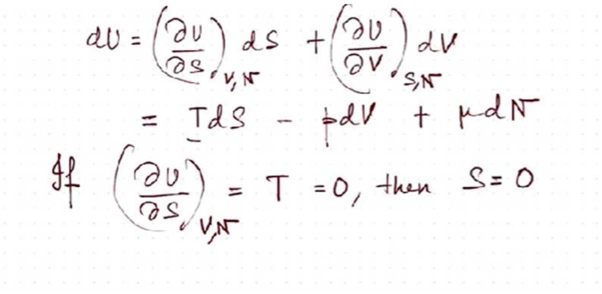
Pressure:

$-\left(\frac{\partial U}{\partial V}\right)_{S, N_1, N_2, \ldots, N_r} = P$

Chemical potential: $\left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_1, \ldots, N_{k \neq j}} = \mu_j$ (j^{th} component)

$$dU = T\,dS - P\,dV + \mu_1 dN_1 + \cdots + \mu_r dN_r$$

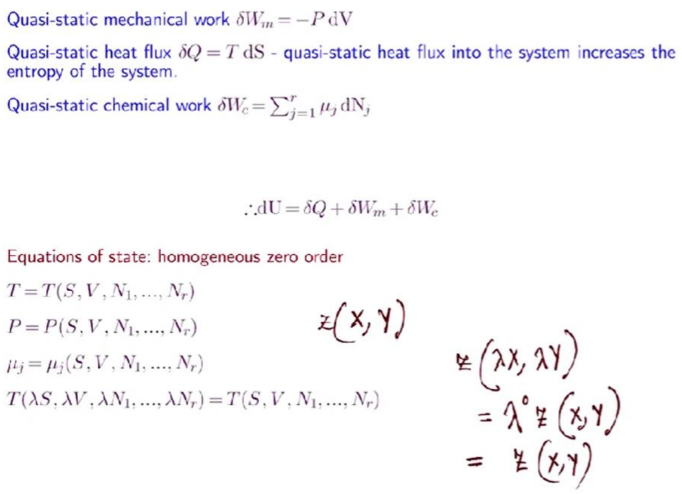
Now, you have defined so basically as s is a continuous differential dynamic amount of the increasing function of u, you can write u also because of continuity and differentiability with respect to the energy you can write u as a function of s v n, right and if you can do that then we have shown and this is exactly what I am writing because it is an exact differential whether it is s, whether it is u because they all depend only on the step system, they depend on the initial and final steps, they do not really depend on the path, so therefore these are all exact differentials. So, if it is an exact differential you can write du for a simple system you can write du because del u del s keeping v n1 and r fixed ds and del u del v keeping dv fixed and then summation i equal to 1 to r del u del ni or del u del nj j equal to 1 to r s v n1 nk which is not equal to j remember so when I write nj here then I am writing j here then what are we fixing we cannot fix j, right because we are changing internal energy with respect to we are changing internal energy with respect to nj so what we are fixing is s v n1 and all the other species concentration or all the other species mole number say for example n1, n2, n3, nk not equal to j up to n and there is an e g, right. So once we have done that now you see del u del s exactly what we told is T del u del s is T and minus del u del v is T, right that is what we have defined and so pressure is the mechanical potential temperature is the thermal potential and chemical potential is del u del nj where s v at n1 and up to nk k not equal to j these are all fixed, right and you get nu j that is the chemical potential of the jth component, right so that is the so now you have this equation and that is the same state rate of compound first law second law which is but it includes now components or chemical species, right. So you have du is T ds minus T dv plus nu 1 dn1 plus nu 2 dn2 similarly plus nu r dv, right now we also know that so again I am repeating del delta w is minus T dv and delta q is T ds this cause making flux the system which increases the entropy of the system and then cause the chemical work then if we define the same way it will be mu dv, right delta wc is j equal to 1 to the power mu j dv, right so you have the heat the thermal work or heat input and then you have the mechanical work and then you have the mechanical work, right. Now if you see these are called equation substrate, right you also require that, right you require T as a function of a s v n 1, P as a function of a s v n 1, right this a s v n 1 to n r these are all excessive variables where T itself is not, P itself is not mu, self is not so if that is so these are called homogeneous zeroth order functions homogeneous zeroth order functions. So basically if I multiply s by lambda v by lambda so basically there is a multiplication factor again I am trying to change by multiplying with lambda what we are doing is we are changing the extent, right we are changing the extensive variable, right extensive variable definitely it will change, right if I make s to lambda s v to lambda v n 1 to lambda n 1 so what we are changing is the extent of the system but remember T does not care about the extent of the system because it is an intensive property or a point function, right it is a point function of all these extensive parameters as a result lambda so this is a homogeneous zeroth order so this is basically so basically what we are trying to say is Z is Z let us not call it Z let us call w as an intensive parameter also v as an intensive parameter no not v, okay let us call small z as an intensive parameter the function of x and y is function of x and y now I write x is changed to lambda and x and this is y that is homogeneous zeroth order which is lambda to the power 0 Z is 1 which is Z, right so it is not so Z which is an intensive here at the small z which is an intensive variable it is not depend on the how much I have changed the extent of x and how much I have changed the this is the y which x and y then x and y are the extensive parameters, right but Z does not change, right so this is something that is very important and this is something that we have explained when we define in this parameters, right in this parameters a point function we can define that point, right so basically this is it is always some sort of a ratio tell you del S for example so these are called potentials and these potentials are if at a point, right you define them at a point and as a result they are homogeneous zeroth order functions of the extensive parameters. Now you can write it in the entropic form, right as I told you that you can write it in terms of S as a function of uvn or u as a function of Svn so here for example I am writing in the entropic form so Ts is del S by del u vn del S by del u is nothing but 1 by T, right it becomes 1 by T, it is identified as 1 by T. Now you have del S del v which is basically minus P by T, del S del u del u del v and del u del v is del u by del v is minus P and del S by del u is minus P by del v is 1 by T so this becomes minus P by del v this is 1 by T minus 2 by T and this is mu by T, del S del n is nothing but del S del u del u del n, right you are using chain rule so you can write this del S del n which is mu by T, right. So you can express the exact differential dS in terms of you know del S del u del S del v and del S del nj are the intensive coefficients, right one is 1 by T, one is minus P by T and mu by T, right. So you have now let us consider what does thermal equilibrium mean.



$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV$$

$$= TdS - pdV + \mu dN$$

If $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = 0$, then $S = 0$



Quasi-static mechanical work $\delta W_m = -P\,\mathrm{dV}$

Quasi-static heat flux $\delta Q = T\,\mathrm{dS}$ - quasi-static heat flux into the system increases the entropy of the system.

Quasi-static chemical work $\delta W_c = \sum_{j=1}^{r} \mu_j\,\mathrm{dN}_j$

$$\therefore \mathrm{dU} = \delta Q + \delta W_m + \delta W_c$$

Equations of state: homogeneous zero order

$T = T(S, V, N_1, \ldots, N_r)$

$P = P(S, V, N_1, \ldots, N_r)$

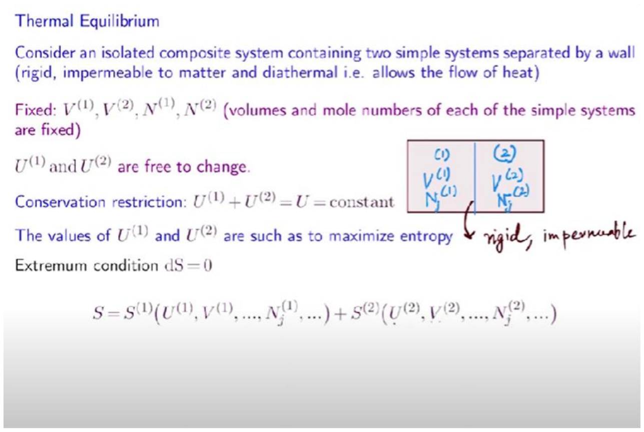
$\mu_j = \mu_j(S, V, N_1, \ldots, N_r)$

$T(\lambda S, \lambda V, \lambda N_1, \ldots, \lambda N_r) = T(S, V, N_1, \ldots, N_r)$

$z(x, y)$

$$z(\lambda x, \lambda y) = \lambda^0 z(x, y) = z(x, y)$$

Now if I have to consider what does thermal equilibrium mean we are basically considering two simple systems, simple system means you are only thinking of internal energy, volume and mole number of species, right of different species. Now you have these two simple, there are two simple subsystems, right these are two simple subsystems we are thinking of two simple subsystems and I have defined this as one is equal to one and this is equal to one and this is equal to two and we have say a single component n1, you can do it for multi components also n1 and n2, you can do it for nj, j equals one to R so you have like R species or R components and see and what we are telling is that we are making this wall, this wall that we have here, this wall is rigid that means it does not adjust with respect to volume changes, right it does not respond to volume changes, right it does not move, it cannot move, it is rigid and then I am telling it also is impermeable that means it cannot, it does not allow any, it does not allow species, does not allow species to move, so it is rigid and impermeable but it is diaphragmatic that means it allows the flow of heat. Now what, see if heat is moving around, right it cannot, it do not allow the flow of matter that means from subsystem one to subsystem two or from subsystem two to subsystem one, no species can flow, right there is no way this can flow because the wall is impermeable to the exchange of species, right exchange of components, right so no, there is no flow of species that is happening, right no mixing of species that is happening, no adjustment of volume that is happening, only thing is diaphragmatic that means it allows the flow of heat as a result internal energy, right which is associated to the flow of heat is going to change, right U1 and U2, right these two terms are free to change, U1 and U2 are free to change. However, the total energy which is U1 plus U2 is constant, right so what we want, we want to see that the values of U1 and U2 are such as to maximize the total entropy, right total entropy and what is total entropy, total entropy is the sum of subsystem entropy, right which is S1, so function of U1, U1 and all this N1, N2, N3 up to NR, similarly S2, U2, V2, S2 again a function of excess parameters of the subsystem, right U2, V2 and all this N, right to NR, right. So now what we are telling is total entropy is S1 plus S2, right which is the function of S1 is the function of U1, U1 and all and S2 is the function of S. Now entropy change, if you think of entropy change which is basically we now write that, so we can write this as dS, dS is nothing but del S1 del U1 dU1 plus del S2 del U2 dU2, however you note that U1 plus U2 is equal to U1, so dU1 plus dU2 that is equal to 0, right. So now you are using dU2 equal to minus dU1, right. So from this you can write dU2 is equal to minus dU1, right. Now you have dS which is del S del U, del S del U is 1 by T, so del S del U for subsystem 1 which is basically 1 by T or more subsystem 1 dU1 plus 1 by T2 and dU2 that is for subsystem 2 but dU2 is equal to minus dU1, right. So I am substituting here, so here I basically write instead of dU2 I write minus and instead of dU2 I put dU1, right that is not it, right. We are substituting dU2 by minus dU1, so if you do that then what happens is you get dS which is equal to dS which is equal to 1 by T1 minus 1 by T2 and dU1. Now dS equal to 0 means 1 by T1 should be equal to 1 by T2, right. So 1 by T1 is temperature in subsystem 1 equals to 1 by temperature in subsystem 2 or we can write consistently that T1 equals to T2, right.


Thermal Equilibrium

Consider an isolated composite system containing two simple systems separated by a wall (rigid, impermeable to matter and diathermal i.e. allows the flow of heat)

Fixed: $V^{(1)}, V^{(2)}, N^{(1)}, N^{(2)}$ (volumes and mole numbers of each of the simple systems are fixed)

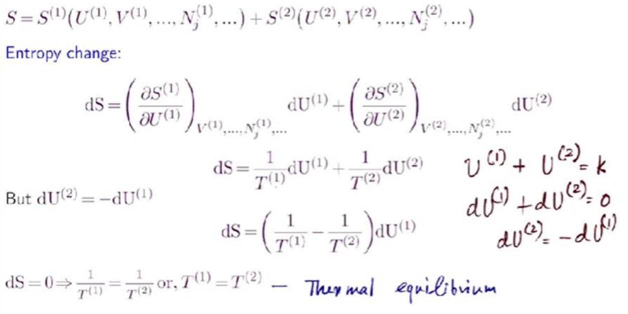
$U^{(1)}$ and $U^{(2)}$ are free to change.

Conservation restriction: $U^{(1)} + U^{(2)} = U = \text{constant}$

The values of $U^{(1)}$ and $U^{(2)}$ are such as to maximize entropy

Extremum condition $\mathrm{dS} = 0$

$$S = S^{(1)}(U^{(1)}, V^{(1)}, \ldots, N_j^{(1)}, \ldots) + S^{(2)}(U^{(2)}, V^{(2)}, \ldots, N_j^{(2)}, \ldots)$$


$$S = S^{(1)}(U^{(1)}, V^{(1)}, \ldots, N_j^{(1)}, \ldots) + S^{(2)}(U^{(2)}, V^{(2)}, \ldots, N_j^{(2)}, \ldots)$$

Entropy change:

$$\mathrm{dS} = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)}, \ldots, N_j^{(1)}, \ldots} \mathrm{dU}^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V^{(2)}, \ldots, N_j^{(2)}, \ldots} \mathrm{dU}^{(2)}$$

$$\mathrm{dS} = \frac{1}{T^{(1)}}\mathrm{dU}^{(1)} + \frac{1}{T^{(2)}}\mathrm{dU}^{(2)}$$

But $\mathrm{dU}^{(2)} = -\mathrm{dU}^{(1)}$

$$\mathrm{dS} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{dU}^{(1)}$$

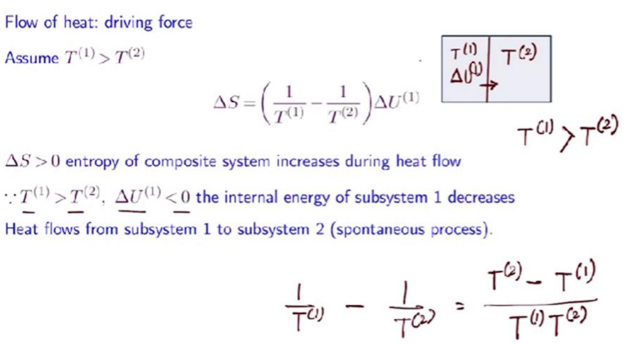
$U^{(1)} + U^{(2)} = k$

$dU^{(1)} + dU^{(2)} = 0$

$dU^{(2)} = -dU^{(1)}$

$\mathrm{dS} = 0 \Rightarrow \frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}$ or, $T^{(1)} = T^{(2)}$ – Thermal equilibrium

So we can immediately write that T1 equals to T2. So this gives you the condition of thermal equilibrium, right and the thermal equilibrium is achieved when there is flow of heat that is allowed. Say for example, if flow of heat is not allowed then there is no T1 equal to T2 because the temperatures cannot change because the internal energies cannot change, right. So as soon as we allow the wall, the heat transfer to occur through the wall then immediately there is this thermal equilibrium that got established and that thermal equilibrium basically is a result of extremization of entropy, right and we will later show that d2S indeed is going to be negative in this case, right. So basically this gives you the thermal equilibrium condition. This is your thermal equilibrium. Remember we are doing, we are taking two subsystems, if you do take n subsystems the same idea will occur. So it will be like if I take system 1, system 2, system 3 and system 4 and in all cases if you have these different walls and all of these walls allow heat exchange then ultimately the equilibrium that we will get, thermal equilibrium that we will get is T1, T1 is equal to T1 is equal to T1 is equal to T1 is equal to T1 is equal to T2 is equal to T3 and T3 is equal to T4, right. But if you put constraint of adiabatic then you will have a temperature gradient and really you will establish a fixed temperature gradient and this temperature gradient cannot change, right. It is a constraint equilibrium, right. But in constraint equilibrium you have all the temperatures to be equal across all subsystems, right. Now this also gives you a way of looking at time forces. Assume that, say for example I have a again I have this system, composite system, let me draw it properly, I have this composite system and that I have this wall and I have T1, T1 and I have T2, right and I am telling that T1 is greater than T2, right that is what we have achieved. Now delta S is 1 by T1 minus 1 by T2 into, right that is what we have found, T S is equal to 1 by T1 minus 1 by T2 into delta S. Now delta S greater than zero, right the entropy of the system increases, right it has to increase, right it cannot decrease during the flow, right. So it has to increase during the flow then delta S has to be greater than zero, right because it increases during, now since T1 is greater than T2 delta U1 has to be less than zero that is delta U1 is the delta U1 is associated with the change in internal energy of the system, right. So since T1 is greater than T2, right T1 is greater than T2, right.



Flow of heat: driving force

Assume $T^{(1)} > T^{(2)}$

$$\Delta S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\Delta U^{(1)}$$

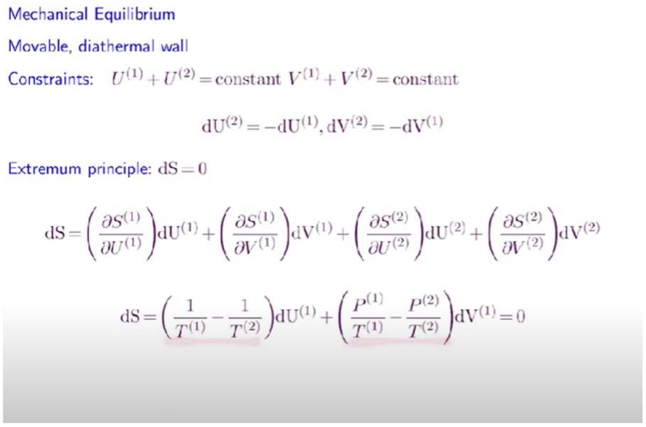
$T^{(1)} > T^{(2)}$

$\Delta S > 0$ entropy of composite system increases during heat flow

$\because \underline{T}^{(1)} > \underline{T}^{(2)}$, $\underline{\Delta U^{(1)}} \underline{<0}$ the internal energy of subsystem 1 decreases

Heat flows from subsystem 1 to subsystem 2 (spontaneous process).

$$\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} = \frac{T^{(2)} - T^{(1)}}{T^{(1)}T^{(2)}}$$



Mechanical Equilibrium

Movable, diathermal wall

Constraints: $U^{(1)} + U^{(2)} = \text{constant}\ V^{(1)} + V^{(2)} = \text{constant}$

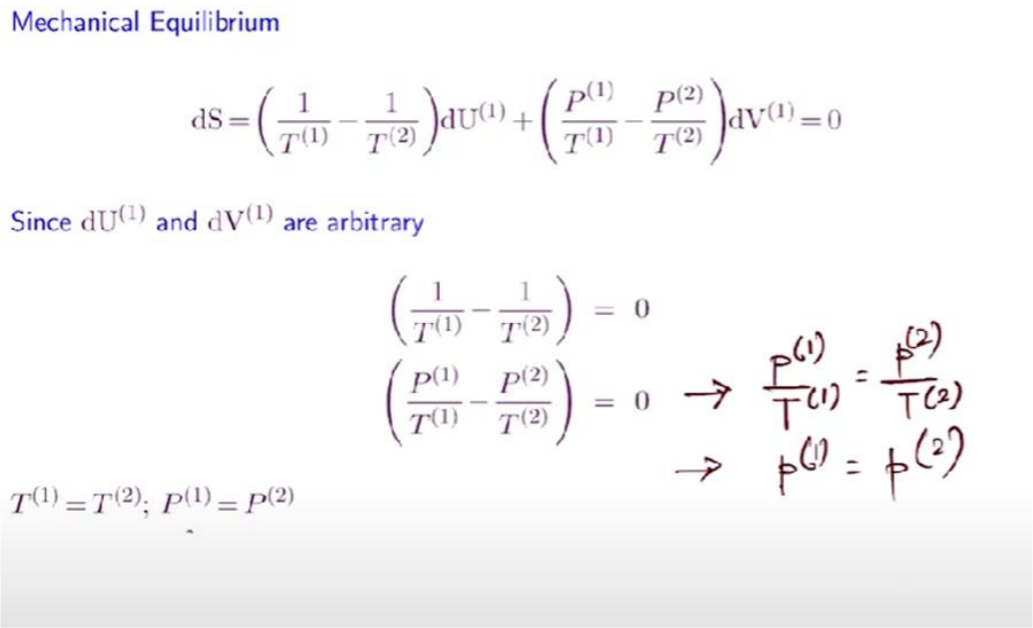
$$\mathrm{d}U^{(2)} = -\mathrm{d}U^{(1)}, \mathrm{d}V^{(2)} = -\mathrm{d}V^{(1)}$$

Extremum principle: $\mathrm{d}S = 0$

$$\mathrm{d}S = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)\mathrm{d}U^{(1)} + \left(\frac{\partial S^{(1)}}{\partial V^{(1)}}\right)\mathrm{d}V^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)\mathrm{d}U^{(2)} + \left(\frac{\partial S^{(2)}}{\partial V^{(2)}}\right)\mathrm{d}V^{(2)}$$

$$\mathrm{d}S = \left(\underline{\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}}\right)\mathrm{d}U^{(1)} + \left(\underline{\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}}\right)\mathrm{d}V^{(1)} = 0$$

So as a result T2 minus T1, so this if I write, so 1 by T1 minus 1 by T2 is equal to T2 minus T1 T2, right and remember this is absolute scale so temperatures are positive for T1, T2. So the denominator is positive but here T1 is greater than T2 therefore T2 minus T1 is negative. So delta U1 has to be negative that means delta U1 that means the internal energy of system 1 which has a higher temperature has to decrease, right and so if it has to decrease that means it has to basically release heat, right and heat has to enter system 2, right. So heat flows from system 1 to system 2 such that the internal energy of system 2 changes to increases and internal energy of system 1 decreases, right. So it gives you our natural heat flow direction also and it also tells you there is a temperature difference that heat flow is such that heat will flow from higher temperature to lower temperature. This is something again from Tauschius inequality we have shown that is the same thing is what we are invoking here and you can see that not only this excrebation of entropy gives you the equilibrium it also gives you the natural reaction for T4, right. So it is a spontaneous reaction for T4. Now think of mechanical so if you now have a if you now have to consider mechanical equilibrium then you make the wall not only diathermal that means not only allow the heat exchange but also make it flexible or movable, right. So we have made it movable. So what are the constraints? The constraints are total U plus U2 has to be constant and V1 plus V2 have to be constant, right. Although Vs can change right for a system subsystem 1 and subsystem 2, V1 plus V2 have to be constant. So dU2 equal to minus dU1, right because U1 plus U2 is constant and similarly dV2 equals to minus dU2. Now again we look at the stream of principle. Now change basically for system 1 is del S1 del U1 del S1 del V1 dV1 plus del S2 del U2 dU2 that is for system 2 and del S2 del V2 dV2. Now del S1 del U1 is 1 by d1 and del S2 del U2 is 1 by d2 and you see there is dU2, dU2 is nothing but minus d1 so you can write 1 by d1 minus 1 by d2. Similarly you can write in this case del S del U again from chain rule what you get is P by T so this becomes P1 by T1 and again here dV2 is written as minus dV1 so therefore there is a minus sign and here is P2 by T2. Now you can see here this has to be equal to 0. Now since dU1 and dV1 can change arbitrarily each of these coefficients this one has to be separated with 0 this one has to be separated with 0. So because the change in U and change in V are arbitrary so this has to be separated with 0 and this has to be separated with 0 so this has to be equal to 0 this has to be equal to 0 so 1 by T1 minus 1 by T2 is equal to 0 basically gives you T1 equal to T2. Similarly now T1 equal to T2 obviously this equation will give you P1 by T1 equal to P2 by T2 and since T1 is equal to T2 is basically gives me P1 equal to T2 that means the pressures in subsistence 1 and 2 have to be equal. When the again they were not equal when we did not allow the volume to change how by making the wall constraint that is rigid we did not allow the wall to move. Now we are making the wall to move and since we are making the wall to move and the total volume is constant we can immediately see that the equilibrium mechanical equilibrium basically means that the pressures in subsistence 1 and subsistence 2 have to be equal apart from temperature so temperature equilibrium is thermal equilibrium and this is the equilibrium pressures the pressures are the same so P1 equal to P2. If there is a pressure gradient then there will be a flow in there will be a change in volume if there is a pressure gradient. So if you create a pressure gradient then there will be a change in volume the wall will start moving and that is what happens even in weather changes and all that if you create a pressure gradient it wants to the overall you want to release this pressure and as a result there is this different in open systems there is this flow work that happens and due to this flow work you get all this rains and stuff so that is that. Now think of chemical equilibrium now think of a rigid again you can impose the condition of rigidity you can impose the condition of rigidity but you make the wall diathermal and permeable to flow of component 1 and impermeable to flow all other components. So we are telling now we are thinking of chemical equilibrium of component 1 so basically I select one membrane which allows component 1 to diffuse or component 1 to transfer between subsystem 1 and subsystem 2 but none other component can and then we are also talking about diathermal volume that is the diathermal volume means we are allowing heat flow right heat flow is allowed and flow of species 1 is allowed. Now if you have that you have 1 by T alpha dU alpha so you have two subsystems again the subsystems are alpha and beta the subsystems are alpha and beta right and it is overall isolated now you have 1 by T alpha dU alpha and mu alpha by T alpha dN alpha dN 1 alpha right we are only allowing flow of species 1 or exchange of species 1 between subsystems alpha and beta and 1 by T beta dU beta plus 1 by mu 1 beta by 2 beta dN beta again dU beta equals to minus dU alpha why because mu alpha since mu alpha plus mu beta is equals to constant similarly N 1 alpha plus N 1 beta is equal to constant so dN 1 beta equals to minus dN alpha so again because we can see from this equation from this equation if you just change dN 1 alpha and this is dN 1 beta which is nothing but minus dN 1 alpha so you have again and dU beta is written as minus dU alpha so you basically rearrange this equation and you get this one and you get 1 by T alpha minus 1 by T beta dU alpha and mu 1 alpha by T alpha minus mu 1 beta by T beta dN 1 alpha right because I have substitute dN 1 beta by minus dN 1 alpha so immediately I get these relations 1 by T alpha plus 1 by T beta which means d alpha by T beta and mu 1 alpha by T alpha plus mu 1 beta by T beta which implies mu 1 alpha equals to minus dN 1 beta by T beta now the chemical as you can see chemical the equilibrium is such that the equilibrium is such that N 1 will change such that the chemical potential of component 1 in alpha sub system should be chemical potential of component 1 in beta sub system right or you can think of this as alpha phase and beta phase and you can see that mu 1 alpha should be equals to mu 1 beta at equilibrium now you can extend it to multi component system so next time I will talk about another important relation called Ginsburg relation so we can see now that for simple systems by just extremization of entropy we can understand the chemical equilibrium the mechanical equilibrium and thermal equilibrium so if you have multiple sub systems say alpha beta gamma so basically or alpha beta gamma delta the equilibrium conditions are like T alpha equals to T beta equals to T gamma equals to T delta similarly mechanical equilibrium is T alpha equals to T beta equals to T gamma equals to T delta and for each species say for example if I allow different species to be permeable to the flow of different species between sub systems we can tell right for each species say I have two species and mu 1 species the component 1 and component 2 so mu 1 alpha equals to mu 1 beta equals to mu 1 gamma equals to mu 1 delta and mu 2 alpha equals to mu 2 beta equals to mu 2 gamma equals to mu 2 beta and so on right if you have R species so you have to solve all of this these are your thermodynamic equilibrium conditions for a simple system where we consider contributions which are chemical mechanical and thermal we are not considering here magnetic or electrical so if you want to extend to that magnetic electrical or surface contribution stuff we have to integrate we have to also incorporate those into our description of equilibrium but here we are considering this equilibrium but what we have found out most important thing is that whether we so that with this very simple axiomatic approach we neither we do not violate any of these laws right and once we do not violate these laws and we satisfy the laws right the total energy cannot change the total mole number is fixed and immediately you can see that what follows are the definitions of thermodynamic equilibrium right what are the thermodynamic equilibrium conditions in terms of thermal so thermal equilibrium chemical equilibrium and mechanical equilibrium right so we get it back so in the next lecture we will start with the one of the other another important description where we will look at Euler equation stuff so till then so let us understand this and absorb this concepts that I have taught and I think this will help you in understanding the overall idea of equilibrium and how to achieve it and this will be a very general this is a very general approach and you can see that you can extend it to multi component multi phase equilibria if there are reactions everywhere you can basically invoke these ideas and you can apply these ideas and you can get your results ok thank you thanks very much



Mechanical Equilibrium

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) dV^{(1)} = 0$$

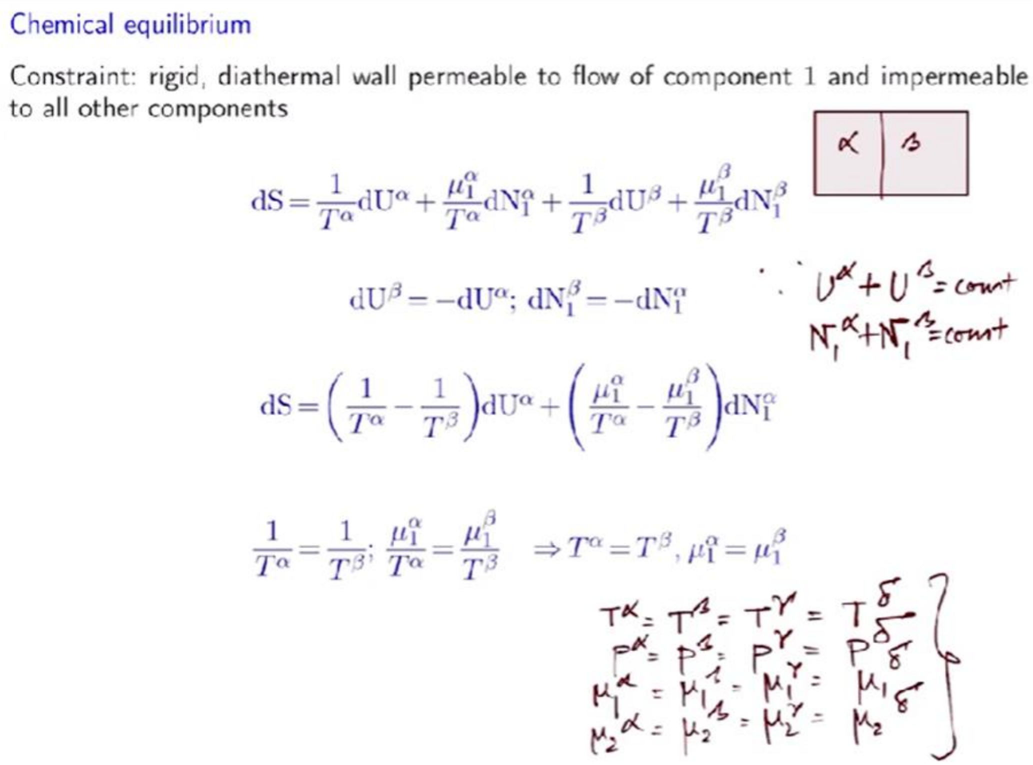
Since $dU^{(1)}$ and $dV^{(1)}$ are arbitrary

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) = 0$$

$$\left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) = 0 \rightarrow \frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}}$$

$$\rightarrow P^{(1)} = P^{(2)}$$

$T^{(1)} = T^{(2)}$; $P^{(1)} = P^{(2)}$



Chemical equilibrium

Constraint: rigid, diathermal wall permeable to flow of component 1 and impermeable to all other components

$$dS = \frac{1}{T^{\alpha}} dU^{\alpha} + \frac{\mu_1^{\alpha}}{T^{\alpha}} dN_1^{\alpha} + \frac{1}{T^{\beta}} dU^{\beta} + \frac{\mu_1^{\beta}}{T^{\beta}} dN_1^{\beta}$$

$$dU^{\beta} = -dU^{\alpha}; \; dN_1^{\beta} = -dN_1^{\alpha} \quad \because U^{\alpha} + U^{\beta} = \text{const}$$

$$N_1^{\alpha} + N_1^{\beta} = \text{const}$$

$$dS = \left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) dU^{\alpha} + \left(\frac{\mu_1^{\alpha}}{T^{\alpha}} - \frac{\mu_1^{\beta}}{T^{\beta}}\right) dN_1^{\alpha}$$

$$\frac{1}{T^{\alpha}} = \frac{1}{T^{\beta}}; \; \frac{\mu_1^{\alpha}}{T^{\alpha}} = \frac{\mu_1^{\beta}}{T^{\beta}} \quad \Rightarrow T^{\alpha} = T^{\beta}, \; \mu_1^{\alpha} = \mu_1^{\beta}$$

$$\left.\begin{array}{l} T^{\alpha} = T^{\beta} = T^{\gamma} = T^{\delta} \\ P^{\alpha} = P^{\beta} = P^{\gamma} = P^{\delta} \\ \mu_1^{\alpha} = \mu_1^{\beta} = \mu_1^{\gamma} = \mu_1^{\delta} \\ \mu_2^{\alpha} = \mu_2^{\beta} = \mu_2^{\gamma} = \mu_2 \end{array}\right\}$$